



Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

The influence of pH on the leaching behaviour of inorganic components from municipal solid waste APC residues

Margarida J. Quina^{a,*}, João C.M. Bordado^b, Rosa M. Quinta-Ferreira^a^a GERSE – Group on Environment, Reaction and Separation Engineering, Department of Chemical Engineering, FCTUC, University of Coimbra, Polo II – Rua Sílvio Lima, 3030-790 Coimbra, Portugal^b Department of Chemical and Biological Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

ARTICLE INFO

Article history:

Accepted 20 May 2009

ABSTRACT

The influence of pH on the leaching behaviour of air pollution control (APC) residues produced in municipal solid waste incineration (MSWI) is addressed in this study. The residue is considered hazardous waste, and in accordance with their chemical properties, the leaching of contaminants into the environment is the main concern. Several leaching tests can be used for research studies or regulatory purposes, where a wide variety of conditions may be tested. Our work deals mainly with the leaching behaviour of toxic heavy metals (Pb, Cd, Zn, Cr, Ni, Cu) and inorganics associated with soluble salts (Na, K, Ca, Cl). The main goal is to obtain an overview of the leachability of APC residues produced in a Portuguese MSWI process. Among the different variables that may have influence on the leaching behaviour, pH of the leachant solution is the most important one, and was evaluated through pH static tests. The acid neutralization capacity (ANC) of the residue was also determined, which is in the range of 6.2–6.8 meq g⁻¹ (for pH = 7) and 10.1–11.6 meq g⁻¹ (for pH = 4). The analysis of the leaching behaviour is particularly important when the leaching is solubility controlled. The amphoteric behaviour of some elements was observed, namely for Pb and Zn, which is characterized through high solubilization at low and high pH and moderate or low solubility at neutral or moderate high pH. The solubility curves for Pb, Cd, Zn, Cr, Ni and Cu as a function of pH were obtained, which are very useful for predicting the leaching behaviour in different scenarios. The solubility of K and Na reveals to be nearly independent of the solution pH and the released amount is mainly availability-controlled. Moreover, the pH static test showed that Cl⁻ is the most pH-independent species. The APC residue turns out to be a hazardous waste because of the high leaching of lead and chloride. On the other hand, leaching of elements like cadmium, nickel and copper is limited by the high pH of the residue, and as long as the waste keeps its ANC, the risk of mobilization of these elements is low.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The process of leaching depends on several physical and chemical factors and occurs whenever a liquid phase percolates or is in contact with a solid material, and inorganic or organic substances are dissolved out (van der Sloot et al., 1997). The most important physical factors are the size, shape and porosity of the particles, homogeneity of mineral phases, temperature, time frame, flow rate or liquid amount of leachant and degree of saturation, and wet/dry cycles. The most important chemical aspects are related with pH and redox conditions, control mechanisms (kinetic or equilibrium), availability for leaching, complexation and sorption processes. The leaching processes may involve precipitation/dissolution, diffusion, sorption, surface coating or wash-off, which may be controlled kinetically or by equilibrium conditions. In order to

evaluate the leaching processes a significant number of tests may be used, depending on the objective: (i) identification of leachable constituents; (ii) classification of wastes; (iii) evaluation, comparison or quality control in waste treatment or products, (iv) field concentration estimates, (v) parameters determination for modelling, (vi) risk assessment (IAWG, 1997). The most important variables that should be established for a specific leaching test are the sample preparation, leachant composition (pH, redox conditions), method of contact, liquid to solid ratio (*L/S*), contact time, temperature and leachant separation method.

In accordance with the Commission Decision 2000/532/EC, which indicates the list of wastes and hazardous wastes, the APC residues are considered hazardous waste. In the literature, several studies are available concerning its leaching behaviour (Eighmy et al., 1995; Bosshard et al., 1996; Iretskaya et al., 1999; Ibáñez et al., 2000; Van Herck et al., 2000; Nagib and Inoue, 2000; Youcai et al., 2002; Shim et al., 2005; Hammy et al., 2005; Mizutani et al., 1996, 2007; Li et al., 2007). The leaching behaviour of bottom ash

* Corresponding author. Tel.: +351 239 798 700.

E-mail address: guida@eq.uc.pt (M.J. Quina).

produced during incineration processes has also been frequently considered (Johnson et al., 1996; Meima and Comans, 1997a,b, 1998, 1999; Kersten et al., 1998; Ibáñez et al., 2000; Meima et al., 2002; Dijkstra et al., 2006, 2008). Some studies addressed inorganic components (Eighmy et al., 1995; Kida et al., 1996; Van der Bruggen et al., 1998; Van Herck et al., 2000; van der Sloot et al., 2001; Abbas and Steenari, 2001; Kosson et al., 2002; Sabbas et al., 2003; Astrup et al., 2005, 2006a,b; Cornelis et al., 2008; Chiang et al., 2009) while others involved organic compounds (Fischer et al., 1992; Hsi and Yu, 2007; Yasuhara and Katami, 2007).

Aqueous solubility is one of the most essential molecular properties, which may determine the environmental fate of contaminants. The pH directly affects the solubility of compounds, mainly of hydroxides and salts containing anions of weak bases. In fact, the pH of leachant that is in contact with the residue, may lead to high variations (several orders of magnitude) in the quantities of contaminants that may be released into the environment as pointed out by several works (Eighmy et al., 1995; Mizutani et al., 1996; Kida et al., 1996; IAWG, 1997; van der Sloot et al., 1997; Van der Bruggen et al., 1998; Kosson et al., 2002; Van Herck et al., 2000; Sabbas et al., 2003).

In general, the leaching tests have a high number of applications in diverse areas such as wastes (bulk, stabilized, solidified, chemical, inert or vitrified), soil (natural, contaminated or compost), sediments (natural, dredge spoils), sludges (industrial, water treatment or sewage) and also construction materials (concrete, aggregates, bricks, tiles, composites, treated wood, or drinking pipes) (van der Sloot et al., 1997). In many respects leaching behaviour is reflected by the pH dependence and this analysis may provide a better understanding of the environmental impact than the analysis of the total elemental composition. Indeed, the leached amount may be in most cases significantly lower than the total content. The total availability is also a parameter of particular interest, which depends on the matrix mineralogy and mineralogical changes in the solution being possible to be significantly lower than the total content (Fallman, 1997). The amount released from a solid into the environment depends also on the solution chemistry and in particular on the oxidation–reduction reactions, complexation reactions, etc. Due to the vast number of leaching tests that may be used for evaluating the leaching characteristics of a waste, it is extremely important to consider an integrated framework. For this purpose, Kosson et al. (2002) indicated a methodology based on a tiered approach, which balances the specificity of the release, the knowledge required, and the resources requested to carry out an evaluation.

Some literature is nowadays underlying that the characterization of waste is entering a new stage, since new developments of leaching tests are being coupled with geochemical modelling (van der Sloot et al., 2006). Indeed, these tools may be used for predicting long-term behaviour of pollutants and major species (Astrup et al., 2006a,b). Concerning the geochemical modelling of the residues produced in the MSWI, a significant number of studies may be found for bottom ashes (Johnson et al., 1996, 1999; Kersten et al., 1997; Meima and Comans, 1997a,b, 1998, 1999; Crannell et al., 2000; Dijkstra et al., 2002, 2006, 2008; Zhang et al., 2008a). Nevertheless, the APC residues have been less considered (Eighmy et al., 1995; Van der Bruggen et al., 1998; Van Herck et al., 2000; Geysen et al., 2004; Astrup et al., 2006a,b; Baciocchi et al., 2006; Yan et al., 2008; Zhang et al., 2008b; Hyks et al., 2009). Although different software may be used for geochemical modelling, by far the most often used is the speciation code MINT-EQA2 (Allison et al., 1991). Finally, it should be noted that geochemical speciation modelling is a powerful tool and may supply diverse information, such as the one related with potential solubility controlling solid phases (Meima and Comans, 1999; Crannell

et al., 2000; Astrup et al., 2006a,b), role of sorption processes (Meima and Comans, 1998, 1999; Dijkstra et al., 2006), and complexation with dissolved organic matter (Dijkstra et al., 2006, 2008; Hyks et al., 2009). According to the classification indicated by Hyks et al. (2009), the elements may be mainly availability-controlled, solubility controlled, or complexation/sorption-controlled. Being the main objective of the present study the analysis of the influence of the pH on the emissions of the principal elements of concern (Pb, Cd, Zn, Cr, Ni, Cu) of APC residues, based on leaching tests, the results obtained were also interpreted with the support of some geochemical modelling literature, in order to identify possible solubility-controlling minerals. This helped to explain the experimental data, and provided information concerning environmental impact assessment or risk analysis. Moreover, soluble salts were also addressed, since the waste is characterized by having high amounts of such species (high quantity of Total Dissolved Solids – TDS).

2. Experimental procedures

In this study, five representative samples of air pollution control (APC) residues collected in a municipal solid waste incinerator located in Portugal were used, and will be further referred to as A1–A5. The APC residues were mainly generated by cleaning gaseous emissions units (semi-dry scrubbers and fabric filters), but include also the fly ash particles carried over from the combustion chamber and collected from the flue gas in the hoppers below the boilers. Then, the APC residues also contain the reaction products and surplus reactants due to the injection of lime slurry and activated carbon in scrubber units to neutralize acid gases and adsorb volatile organic compounds (e.g. dioxins) and volatile heavy metals. These samples were characterized in a previous work, in respect to the main physical, chemical and mineralogical properties (Quina, 2005; Quina et al., 2008a).

The study of the influence of pH was mainly based on prEN 14429, which specifies a pH dependence leaching test in order to identify the leaching behaviour of granular materials under certain pH conditions, and for brevity may be referred to as “pH static leach test” (van der Sloot et al., 2007). The test consists on a set of parallel batch extractions of the material at $L/S = 10$ (L kg^{-1}) in closed flasks, where sub-samples of material (25 g) are in contact with aqueous solutions with increasing quantities of HNO_3 for 48 h under agitation, prior to the measurement of pH for the titration plots. The pH end points shall be in the range of 4–12, and the analysis of contaminants in the leachate can be used to assess their leachability at pH values of interest.

In addition, the test indirectly provides a measure of the acid neutralization capacity (ANC), which corresponds to the ability of the material to neutralize acids (due to any species that can accept and neutralize protons). The total elemental content (TC) of those elements was determined by acid digestion. The total availability (TA) was determined according to the Dutch availability test (NEN 7341), which allows the quantification of the release amounts that leach out when the waste is exposed to extreme conditions, such as very long period, disintegration of the material, or after loss of acid neutralization capacity in an aerobic ambient. This method involves two consecutive extractions with a liquid to solid ratio (L/S) of 50 L kg^{-1} at pH 7 and at pH 4. The test DIN 38414-S4 is a German standard batch leaching test used to determine the leaching of sediments and sludges and includes an extraction at $L/S = 10$, by shaking the suspension for 24 h with demineralised water.

The metals considered in this study were Pb, Cd, Zn, Cr, Ni, Cu, Na, K and Ca and were determined by flame atomic absorption spectroscopy (FAAS), Perkin Elmer 3300, using hollow cathode

lamps and air-acetylene flame. Chlorides and sulphates were quantified by ionic chromatography, Action Analyser- Waters, with a 100 μL loop. However, when a large amount of HNO_3 was added for pH control, the chloride concentrations were obtained by titration with AgNO_3 using K_2CrO_4 as indicator. This classic method of analysis reveals reliable results, since chlorides are generally present in high concentrations.

The reagents that were used have pro analysis grade being the leaching tests performed with demineralised water.

3. Results and discussion

The main objective of this study is focused on the analysis of the influence of the pH on the emissions of the principal elements of concern (Pb, Cd, Zn, Cr, Ni, Cu) of air pollution control (APC) residues. Moreover, soluble salts were also addressed, since the waste is characterized by having high amount of such species (high quantity of Total Dissolved Solids – TDS).

3.1. pH evolution and acid neutralization capacity (ANC)

In accordance with prEN 14429, at least eight different final values of pH are required, covering the minimum range of 4–12. In this study, only acid (HNO_3) was needed to cover that range, since the natural pH of APC residues (pH that results from the contact of the residue with water) is higher than 12 for all samples (A1–A5). As an example, Fig. 1 shows the results obtained for pH in the leachant for four defined stages, up to 4, 22, 44 and 48 h. In this case 13 pre-determined quantities of acid (HNO_3) were added to achieve the desired end pH values. The results show that 4 h is not enough to obtain equilibrium conditions, mainly for volumes of acid higher than 30 mL. For small additions of acid corresponding to pH higher than 12, equilibrium conditions are easily attained by the leachant solution, mainly due to the high quantities of $\text{Ca}(\text{OH})_2$, CaSO_4 and CaOHCl . Nevertheless, at the end of the test, equilibrium conditions were observed for all the pH range. Indeed, the pH difference detected at $t_0 + 44$ h and $t_0 + 48$ h did not exceed 0.3 pH units.

The capacity of a certain material to neutralize acids (acid neutralization capacity – ANC), is a key property for understanding its long-term behaviour, since precipitation/dissolution of metals is directly affected. The amount of acid added in each solution was converted into equivalents of acid per dry weight of the material in order to obtain ANC. Fig. 2 shows the titration curves for four different industrial samples (A2–A5). The ANC shall be reported to a reference pH, and in our case two values were considered: pH = 7 (referred to $\text{ANC}_{\text{pH}7}$) and pH = 4 ($\text{ANC}_{\text{pH}4}$). These results

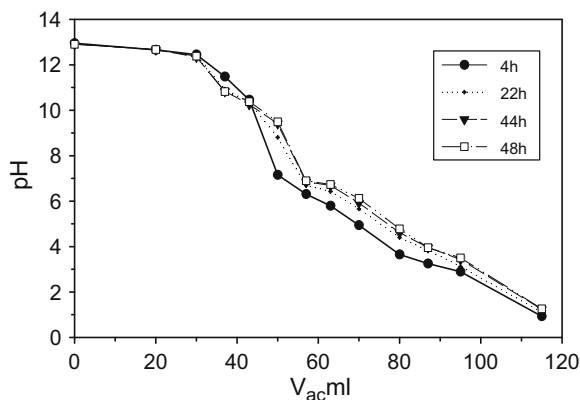


Fig. 1. pH evolution as a function of the volume of acid added to the leachant for 4, 22, 44 and 48 h.

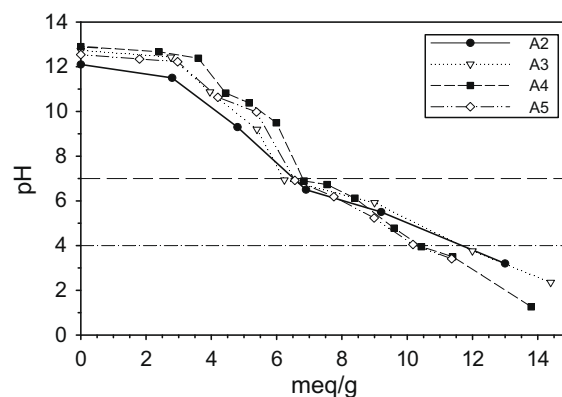
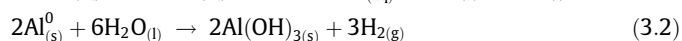
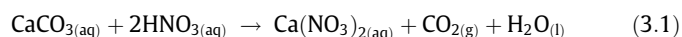
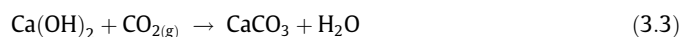


Fig. 2. Equivalents of acid per gram of residue for samples A2–A5.

show that 6.2–6.8 meq g^{-1} were added in order to reach pH = 7 while for pH = 4 this amount increased to 10.1–11.6 meq g^{-1} . From our previous studies related with the determination of the total availability (standard NEN 7341), the estimated ANC was $\text{ANC}_{\text{pH}7} = 4.2\text{--}6.3 \text{ meq g}^{-1}$ and $\text{ANC}_{\text{pH}4} = 7.6\text{--}9.3 \text{ meq g}^{-1}$ (Quina et al., 2008a). Therefore, the values observed now in Fig. 2 reveal that the total availability test underestimated the ANC for the APC residues being possible to strengthen that the residue exhibits high resistance to pH variations. Depending on the considered element, the high ANC of the APC residue may have a positive (e.g. Cd) or a negative (e.g. Pb) effect on the leaching behaviour in terms of environmental impact. In fact, the high ANC combined with high natural pH of APC residues (higher than 12) leads to low releases for Cd and high for Pb. These features will be further explained in the following section. High quantities of gases were released when the acid solutions were added to the solid phase, which may correspond to CO_2 (from the dissolution of the carbonates) and H_2 (from the reaction with elemental metals, mainly aluminium) taking into account the characteristics of the residue:



Calcium carbonate may be formed in the residue according to Eq. (3.3). This reaction may occur in the gaseous cleaning units (Baciacchi et al., 2006), where high quantities of calcium hydroxide are used for gaseous acid neutralization, being also possible to be considered as an aging reaction (IAWG, 1997):



For safety reasons, some references in the open literature stress the importance of hydrogen gas releasing when the APC residues are disposed of (Sabbas et al., 2003; IAWG, 1997). In spite of the significant dependence of ANC on the technology industrially used for gaseous emissions control, some published works indicate similar values to the ones determined in our case (Poletti et al., 2001).

3.2. The influence of pH on the leaching behaviour of toxic heavy metals

Although MSW incineration has as main objective the destruction of organic matter, solid residues with a potential negative impact on the environment are also produced. The harmful consequences on the soil and groundwater of APC residues are mainly due to the presence of toxic heavy metals (Pb, Cd, Zn, Cr, Ni, Cu), whose amounts and chemical speciations are mainly dependent on the feed stock composition, operating conditions in the combustion chamber, vapour pressure of the metals, and technologies used for air pollution control (APC). Among those elements, Cr,

Ni and Cu may be considered as lithophilic, since their most common compounds have boiling points above 1500 °C, being consequently their concentrations in APC residues quite reduced. On the contrary, Pb, Cd and Zn are usually considered as volatile metals, and so considerable concentrations may be found in the APC residue.

In order to analyse the influence of the pH on the leaching behaviour of heavy metals, the leaching method described in Section 2 was carried out and the eluates were subsequently characterized to determine the heavy metals concentrations. For comparing the concentrations of Pb, Cd, Zn, Cr, Ni and Cu in the eluate as a function of pH, other quantities were also included in Fig. 3a–f: the total elemental content (TC), the total availability (TA) and the quantity leached in the standard test DIN 38414-S4. The range of TC, TA and DIN 38414 leaching for Pb, Cd, Zn, Cr, Cd

and Ni obtained in five representative industrial samples of APC residues (A1–A5) are indicated in Table 1, being these values included in Fig. 3a–f. These data show that the highest concentration in terms of toxic heavy metals is the one for Zn followed by Pb, whereas the most available elements for leaching (TA) are Zn and Cu. Moreover, when the waste is in contact with water (DIN 38414), Pb is the major problem. In addition, the legal limits established by the Portuguese legislation (in accordance with EU) for disposal in hazardous waste landfills (tested through DIN 38414-S4) were also represented in those figures. The experimental data were fitted to polynomial curves for each element according to Eq. (3.4) and the numerical values obtained for the corresponding coefficients are indicated in Table 2. These curves are the ones represented in Fig. 3a–f by solid lines (marked with fitting), being usually referred to as pH solubility curves:

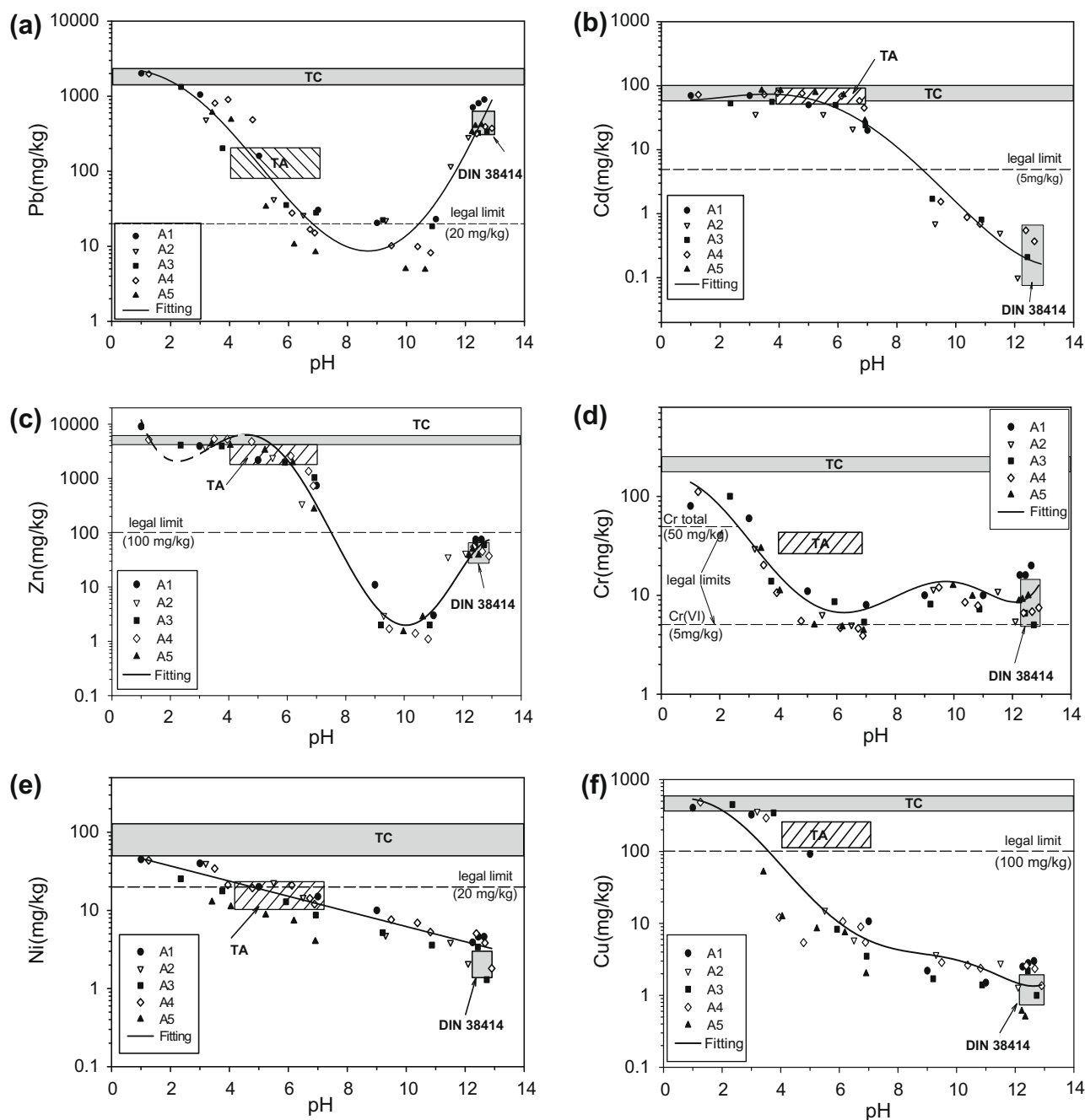


Fig. 3. Influence of pH on the leaching behaviour of (a) Pb; (b) Cd; (c) Zn; (d) Cr; (e) Ni; and (f) Cu.

Table 1

Range of TC, TA and leaching with DIN 38414 for five different samples of APC residues.

	TC		TA		DIN 38414	
	Min–Max	Mean	Min–Max	Mean	Min–Max	Mean
Pb (mg/kg)	1853–2408	2143	94–216	142	324–483	435
Cd (mg/kg)	57–87	72	48–86	65	0.15–0.2	0.18
Zn (mg/kg)	4308–6367	5416	1700–4360	2936	43–63	49
Cr (mg/kg)	188–259	225	24–45	32	5.9–7.3	6.4
Ni (mg/kg)	60–132	103	9–26	18	0.1–2.5	1.7
Cu (mg/kg)	456–648	555	115–288	210	0.2–2.0	1.1

$$\log(\text{Conc}) = a_0 + a_1\text{pH} + a_2\text{pH}^2 + a_3\text{pH}^3 + a_4\text{pH}^4 + a_5\text{pH}^5 + a_6\text{pH}^6 \quad (3.4)$$

Such solubility curves may be useful for compliance comparison or modelling analysis.

The behaviour of Pb in aqueous solution was plotted as a function of the pH in Fig. 3a, where all the information referred to above was also included (TC, TA and DIN 38414). The amphoteric nature (“V” shape) is well observed, with high solubility occurring at low and high pH values. The results show that the total elemental quantity TC in the residue is 1853–2408 mg kg^{−1} (Table 1), and the released amount may vary several orders of magnitude in function of the pH. The amounts released in the total availability test (pH = 7; pH = 4) are in the range of 94–216 mg kg^{−1}, and for extractions with water (standard DIN 38414) the extracted amount may attain 324–483 mg kg^{−1}. For this reason, it is common to refer that the availability test fails for Pb, since under aggressive conditions the extracted quantity is lower than when the leachant is only water. The values obtained through the availability test are quite consistent with the solubility curve (solid line), even though these results are not expected to match, because the *L/S* value of the TA test is much higher than the pH static test (*L/S* = 50 for each extraction vs. *L/S* = 10). Therefore, probably the duration of the TA test (3 h for each extraction) is too short to attain equilibrium for Pb, as indicated in the literature for similar residues (bottom ash) (Dijkstra et al., 2006). The results achieved throughout DIN 38414 (compliance test) are in entire agreement with the solubility curve (in this case *L/S* is 10 with a duration of 24 h), and since the legal limit of 20 mg kg^{−1} is largely exceeded, the residue should be considered hazardous. It is important to note that the natural pH of the residue, in a suspension of 10 L kg^{−1}, is higher than 12, and therefore this material will hardly comply with the regulatory threshold without treatment. Indeed, lead is the most challenging heavy metal in what regards the potential environmental impact of the residue. For pH lower than 2 the amount of Pb released is close to TC, and therefore its total elemental content may be easily determined with acid solutions. The experimental values obtained for this element are in agreement with the ones indicated in the literature for similar residues (Eighmy et al., 1995; Mizutani et al.,

1996; IAWG, 1997; Van der Bruggen et al., 1998; Van Herck et al., 2000; van der Sloot et al., 2001). The results clearly show that the emission of Pb is solubility controlled being its quantity in the liquid phase limited by different minerals that depend on the pH of the solution. Geysen et al. (2004) refer to that, according to simulations with Visual Minteq for a very similar MSWI APC residue (with comparable total elemental content as well as the main crystalline mineral phase), the main controlled phases are: Pb₂(CO₃)Cl₂ for pH 4–6; PbClOH for pH 6–12; and Pb₄(OH)₆SO₄ for pH > 12. If no sulphate is available for leaching, the Pb solubility above pH 12 may be controlled by Pb₂(OH)₃Cl instead of Pb₄(OH)₆SO₄. By comparing the simulation curves obtained by Geysen and co-workers with the solubility curve obtained in our study, a satisfactory agreement was observed. Astrup et al. (2006a,b) investigated also the leaching of APC residues by geochemical speciation modelling in the absence of high salt levels with and without carbonation effect. Under these conditions, Pb seems to be controlled by Pb₂V₂O₇ for pH below 8–9, and Pb₂O₃ for pH above 9. Cerrusite (PbCO₃) may also have a role on the Pb solubility. This phase was also described by Eighmy et al. (1995) for Electrostatic Precipitator (ESP) residues at pH 8–10, and in addition anglesite (PbSO₄) was indicated as controlling solid at pH 3–8 as well. Moreover, Van der Bruggen et al. (1998) analysed ESP residues from MSWI, and according to MINT-EQA2 modelling, Pb₅(PO₄)₃Cl is the solubility controlling phase for pH lower than 9, whereas Pb(OH)₂ is the one observed for higher pH values. Similar results were indicated by Yan et al. (2008) and Van Herck et al. (2000). However, Van Herck and co-workers indicated that Pb₅(PO₄)₃Cl controls the solubility only for pH < 3.5, while for pH between 3.5 and 9 the controlling mineral is Pb(OH)₂·Al(OH)₃·2AlPO₄·H₂O, and for pH > 9, Pb(OH)₂ is again indicated. It should be stressed that Pb leaching may be also influenced by sorption processes, being this element referred to in some studies as a sorption/complexation-controlled element (Hyks et al., 2009). In fact, at high pH (>11), Pb cations (as well as Ni and Cd) tend to sorb into reactive surfaces such hydrous iron (hydr)oxides and hydrous aluminium (hydr)oxides. On the contrary, Yan et al. (2008) pointed out that the leaching of Pb (and Cd) is controlled by dissolution/precipitation mechanism, whereas Zn and Ni are dependent on surface adsorption reactions. The sorption of Pb has been underlined in several studies involving MSWI bottom ashes (Kersten et al., 1997; Meima and Comans, 1998, 1999; Dijkstra et al., 2002, 2006, 2008). However, Zhang et al. (2008a) refer to that surface complexation modelling has little effect on Pb leaching and that the precipitation/dissolution modelling allowed good adjustment to the experimental values. At pH above 8, the controlling phase is Pb(OH)₂, and at pH below 8, Pb₅(PO₄)₃Cl is the one that is identified.

The leaching behaviour of cadmium as a function of pH is depicted in Fig. 3b, which has a distinct shape when compared with lead. In fact, for Cd the amphoteric behaviour is not observed. In this case, when pH is lower than 6 almost all Cd is released, and

Table 2

Polynomial coefficients for pH curves for Pb, Cd, Zn, Cr, Ni and Cu.

Coefficient	Pb	Cd	Zn	Cr	Ni	Cu
<i>a</i> ₀	3.3850	1.8095	6.5334	2.2157	1.7626	2.7442
<i>a</i> ₁	−0.0265	−0.0889	−3.6345	−2.7468 × 10 ^{−8}	−0.0969	−1.3927 × 10 ^{−8}
<i>a</i> ₂	1.9130 × 10 ^{−9}	0.0701	1.3447	−0.0547		0.0260
<i>a</i> ₃	−0.0227	−0.0134	−0.1670	−0.0258		−0.0540
<i>a</i> ₄	3.3614 × 10 ^{−3}	5.642 × 10 ^{−4}	1.3378 × 10 ^{−10}	8.9148 × 10 ^{−3}		0.0114
<i>a</i> ₅	−1.4385 × 10 ^{−4}		1.0783 × 10 ^{−3}	−8.5171 × 10 ^{−4}		−8.9502 × 10 ^{−4}
<i>a</i> ₆	1.5148 × 10 ^{−6}		−4.5192 × 10 ^{−5}	2.6198 × 10 ^{−5}		2.4355 × 10 ^{−5}
<i>r</i>	0.94	0.97	0.98	0.79	0.87	0.92
<i>n</i>	58	42	44	58	52	48

r – Correlation coefficient; *n* – number of experimental determinations considered.

for pH higher than 7 the released amount decreases more than three orders of magnitude. When pH is higher than 12, Cd concentration is difficult to measure with flame atomic absorption spectroscopy (FAAS), once those values are in the range or even lower than the detection limit. In these cases, the graphite furnace is the recommended analytical technique. The low solubility of Cd for high pH makes this element not a critical one when the residue is in contact with water, in spite of its low legal threshold (5 mg kg^{-1}) as a consequence of its high toxicity. The results measured in the leachates from DIN 38414 tests show some dispersion, which is explained by the fact that the concentrations correspond to the region of the detection limit of FAAS ($\text{DL} = 0.022 \text{ mg L}^{-1}$). The results show clearly that the emission of Cd is solubility controlled, and their concentrations in the liquid phase are limited by different mineral depending on the pH. For Electrostatic Precipitator (ESP) ash Van der Bruggen et al. (1998) and Van Herck et al. (2000) have considered that otavite (CdCO_3) is the main controlling solid phase for pH lower than 12 and Cd(OH)_2 for pH higher than 12. Van Herck et al. (2000) suggest that at pH 12 the mineral $\text{Cd}_4(\text{OH})_6\text{SO}_4$ may also play an important role. In fact, our results were compared with the simulation curves obtained by these authors (results not shown in this paper) and a very good agreement was observed. Also Yan et al. (2008) identified $\text{Cd}_4(\text{OH})_6\text{SO}_4$ at pH 9–12, and Cd(OH)_2 at pH 12–14 as the mineral solid phases that control Cd solubility. The role of otavite for pH 5–10 was also referred to by Eighmy et al. (1995). Some studies indicate that at high pH (>11) Cd tend to sorb into reactive surfaces of APC residues such as hydrous iron (hydr)oxides and hydrous aluminium (hydr)oxides (Hyks et al., 2009). Yan et al. (2008) justified the difference of experimental and simulated data at pH 10–12, as a consequence of no adsorption (surface complexation) was admitted in the model. The leaching of Cd is described satisfactorily by the surface complexation model over a large pH range for MSWI bottom ashes (Meima and Comans, 1998; Dijkstra et al., 2006, 2008). These studies mention that otavite (CdCO_3) is too soluble to describe the observed Cd concentration. Zhang et al. (2008a) used a precipitation/dissolution modelling and determined that the controlling solids for Cd in bottom ashes are $\text{Cd}_4(\text{OH})_6\text{SO}_4$ for pH 9–11 and Cd(OH)_2 for pH 11–14. They pointed out that when only precipitation/dissolution reactions were used, the modelling results greatly overestimated the leaching concentration of Cd for pH 6–12. When the surface complexation model was applied, the modelling results fitted well the measured values over a large pH range. In the pH range 6–12, a part of the Cd was adsorbed by hydrous ferric oxide (Fe(OH)_3 and FeO(OH)). An important characteristic of Cd indicated in the literature is its tendency to form soluble chlorides complexes (e.g. CdCl_4^{2-}) (IAWG, 1997; van der Sloot et al., 1997). Thus, considering the high concentration of chlorides in the solutions, it is likely that Cd was mobilized due to the possibility of forming that anionic complex. Yan et al. (2008) showed that using dissolution/precipitation modelling the main forms of Cd in the solution at pH lower than 9 are CdCl^+ and $\text{CdCl}_2(\text{aq})$ (accounting for about 98% of total dissolved forms). For pH 10–14, Cd is dissolved mainly as CdOH^+ , $\text{Cd(OH)}_2(\text{aq})$, Cd(OH)_3 and Cd(OH)_4^{2-} .

The leaching behaviour obtained for zinc is indicated in Fig. 3c for five samples of APC residues. Although the total elemental content of this element in the residue is in the range of 4308–6367 mg kg^{-1} (Table 1), the leaching concentration shows to be strongly dependent on the pH of the solution due to the high solubility control. For this element, the amphoteric characteristics are also well observed, since it exhibits high solubility at both low and high pH values. In fact, the released amount may vary four orders of magnitude when the pH is in the range of 1–13. Also in this case the results for total availability tests (pH 4 and 7) and according DIN 38414 are in close agreement with the curve of solubility. The regulatory threshold for Zn is 100 mg kg^{-1} , and

therefore, this element complies with the legislation. The quantifications of Zn through FAAS were time consuming since the linear range is about $0\text{--}1 \text{ mg L}^{-1}$, and dilutions higher than 500 were required for some samples, which may introduce some quantifications errors. In order to understand the solubility curve of Zn indicated in Fig. 3c our results may be supported by the literature, namely by those studies involving geochemical modelling. Van der Bruggen et al. (1998) have considered ESP residues from MSWI and found that for example at pH 6, one third of the total elemental Zn remains in solution, about one third is precipitated as smithsonite (ZnCO_3) and one third as $\text{ZnO}\cdot\text{SiO}_2$. The solid $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ is the controlled phase at pH 6–8 and ZnO at pH 7–13. At low pH, the equilibrium concentration is determined by the maximum amount of zinc that leaches from the waste. When pH is higher than 13, Zn solubility increases, mainly due to the formation of hydroxide complexes. Van Herck et al. (2000) indicated similar results for Zn, but in this case all the solubility curve is controlled by $\text{ZnO}\cdot\text{SiO}_2$, ZnCO_3 and Zn(OH)_2 . Similarly to the Cd, our results were compared with the simulation curves obtained by Van Herck and co-worker (results not shown in this paper) and again, a good agreement was observed. Eighmy et al. (1995) demonstrated that the leaching of zinc may be modelled with smithsonite (ZnCO_3) over pH 5–10 and ZnSiO_3 at low pH values (3–5). Yan et al. (2008) referred to that in this case only dissolution/precipitation simulation is enough to be in agreement with experimental results, which means that adsorption (surface complexation) is not important. The dominant species in solution are Zn^{2+} and ZnCl^+ for pH 0–6; ZnSiO_3 , ZnOH^+ , $\text{Zn(OH)}_2(\text{aq})$, Zn(OH)_3^- , and Zn(OH)_4^{2-} for pH 7–13 while above pH 14 the amount of Zn(OH)_2 decreased. In this study the main controlling solid is ZnSiO_3 . Other works refer to that at high pH, Zn do not tend to sorb to reactive surfaces of APC residues such as hydrous iron (hydr)oxides and hydrous aluminium (hydr)oxides (Hyks et al., 2009). Astrup et al. (2006a,b) identified as main controlling phases the mineral willemite (Zn_2SiO_4) in the region of pH 7 and in the pH range of 8–10 is zincite (ZnO) that may play an important role on solubility. At pH 10.5–12, some outliers were described by calcium zincate ($\text{CaZn}_2(\text{OH})_6\cdot 2\text{H}_2\text{O}$), which is a solid solution of Zn in portlandite. Below pH 7, Zn seems to be undersaturated with respect to willemite, and the solubility control may be ZnSiO_3 . The leaching of Zn is well described by the surface precipitation model over a large pH range for MSWI bottom ashes (Meima and Comans, 1998; Dijkstra et al., 2006, 2008; Zhang et al., 2008a). Though, a good description of Zn solubility is also obtained by willemite (Zn_2SiO_4) (Dijkstra et al., 2006). Also for bottom ash, Dijkstra and co-worker found that zincite (ZnO) is too soluble to explain Zn leaching at high pH. They refer that additional research is required to confirm whether Zn minerals or adsorption processes are responsible for Zn leaching from MSWI residues. Other important conclusion of this study is the strong time dependency of this element in the pH 4–8 region. Zhang et al. (2008a) indicated that Zn precipitated mainly as ZnCO_3 for pH 5–8 and as ZnO for pH values above 8.

The observed behaviour for chromium as a function of pH is illustrated in Fig. 3d where total chromium concentrations were represented, since FAAS was used for quantifications. It is important to note that the toxicity of Cr depends on the oxidation state, being well known that Cr(VI) is more toxic than Cr(III). The legal limit for Cr-total was not exceeded in leachates from DIN 38414 tests. However, if chromium in solution is mainly Cr(VI), the residue may have a significant negative impact on environment, since the limit for Cr(VI) is now exceeded for all DIN 38214 testes. It should be noted that Cr(III) compounds are sparingly soluble, and therefore, Cr(VI) compounds are predominant (Cornelis et al., 2008). For chromium the amount released during the total availability (TA) test is higher than the one predicted through the solubility curve. The observed differences may be due to the fact

that in the case of the total availability test, the liquid to solid ratio (L/S) is 50 L kg^{-1} in both extractions (for pH 7 and 4). Contrarily, in the case of the pH static test the L/S ratio is 10 L kg^{-1} , and this is also an important parameter in the case of solubility control. In a recent review (Cornelis et al., 2008), the leaching mechanisms of oxyanionic metalloid in alkaline solid wastes was analysed. In fact, chromium is a redox-sensitive element, but only Cr(VI) is relevant for alkaline wastes in the context of leaching. Indeed, the leaching of Cr is very dependent on the redox state at which it occurs in the solid matrix. This work also refers to that mechanisms such as surface adsorption and solid solution formation with minerals containing Ca may be found in all alkaline waste types. The adsorption by Fe and Al oxides will only be important in weathered wastes. This oxyanion may be uptake on ettringite, monosulphate and hydrocalumite by forming solid solution phases being this mechanism important for leaching control. Other important conclusion reported is the low overall reductive capacity of APC residues, due to the low quantities of oxidable compounds (non-combusted organic matter, ferrous and metallic Fe, Al or sulphides). Based on literature, some information is found concerning the geochemical modelling of Cr. Thus, according to Van der Bruggen et al. (1998), for ESP ash, Cr may precipitate as FeCr_2O_4 at pH 4–12 and as Cr_2O_3 at pH > 12. Eighmy et al. (1995) identified PbCrO_4 as the controlling solid at pH 5–9. Astrup et al. (2006a,b) evaluated APC residues leaching data and also observed that crocoite (PbCrO_4) adequately described the Cr concentrations at pH below 8–9. Above this pH, $\text{Ba}(\text{S,Cr})\text{O}_4$ may control Cr solubility. The decrease in Cr concentrations at high pH could be caused by incorporation of Cr(VI) into low solubility minerals (e.g. ettringite). Moreover, $\text{Ba}(\text{S,Cr})\text{O}_4$ phases may have some contribution in the solubility at high pH. In the range of pH 4.5–8.5 the Cr(IV) may be reduced by Al^0 of the APC residues. It is important to note that Cr(VI) is present as an anion and sorption at low pH values may be important. However, some anions such as SO_4^{2-} may reduce the sorption effect. Hyks et al. (2009) stressed that at high pH and oxidizing conditions, chromium is likely to form CrO_4^{2-} , becoming then rather mobile since sorption to iron (hydr)oxides and hydrous aluminium (hydr)oxides can be excluded. This study showed that for fly ashes, 2 minerals control Cr release: Cr-containing analogue of ettringite ($\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) and $\text{Ba}(\text{S,Cr})\text{O}_4$ solid solution. For semi-dry APC residues this pattern was not observed. Zhang et al. (2008a) indicated that for MSWI bottom ash, the precipitation/dissolution modelling describe well the behaviour of Cr at pH 7–12, being Cr_2O_3 the solid phase that control their leachability. At pH 3–7, this work showed that surface complexation had an important role on Cr leaching. In fact, a certain amount of Cr may be absorbed by FehOCrOH^+ . Therefore, for modelling the behaviour of Cr as a function of pH both precipitation/dissolution and surface complexation should be used. According to Sperling et al. (1992), the predominant chemical species in solution for Cr(VI) are CrO_4^{2-} at pH above 7 and HCrO_4^- at pH below 6. The Cr(III) is almost insoluble for pH greater than 5. The main reducing agents for chromium are Fe(II), organic compounds, sulphides and MnO_2 . The chromate ions are stable when pH and redox potential are high (Abbas and Steenari, 2001). Sabbas et al. (2003) refer that in alkaline conditions the Cr(III) may be rapidly oxidized to Cr(VI) with O_2 , but high values of the redox potential are required.

The behaviour of Ni is shown in Fig. 3e, when the pH of the solution was varied in a broad range. The total content for this element can be from 60 up to 132 mg kg^{-1} , and the total availability (TA) and the results from DIN 38414 tests as well are in accordance with the solubility curve. The released amounts observed when the residue contacts with water (test DIN 38414) are well below the regulatory limit (20 mg kg^{-1}) for considering the waste hazardous. The geochemical modelling analysis regarding Ni is limited. However, Yan et al. (2008) showed that for MSWI fly ash the

modelling results by using Visual MINTEQ are in good agreement with the experimental leaching data at pH 7–14, being the $\text{Ni}(\text{OH})_2$ the controlling phase. For pH 4–8, the experimental values are lower than those predicted through modelling, and thus the surface adsorption reaction may play an important role. For MSWI bottom ash, Zhang et al. (2008a) pointed out that the behaviour of Ni including both precipitation/dissolution and surface complexation should be used for modelling. In this case, the element is also mainly controlled by $\text{Ni}(\text{OH})_2$ if pH is in the range 7–14 while at pH 6–9, the adsorption by FehONi^+ and FeONi^+ revealed to play an important role. Dijkstra et al. (2006, 2008) showed also for bottom ash that at pH 4–8 the leaching of Ni may increase due to slow desorption and at pH 10–12, $\text{Ni}(\text{OH})_2$ may be the controlling phase.

In respect to copper, the results obtained with different pH values were plotted in Fig. 3f. For this element the total content for the five samples were in the range $456\text{--}648 \text{ mg kg}^{-1}$, and the limit of 100 mg kg^{-1} established for the release according DIN 38414 was not exceeded. Eighmy et al. (1995) compared geochemical modelling predictions through MINTEQA2, with experimental leaching data for Cu and a very good agreement was found, by considering that $\text{Cu}(\text{OH})_2$ is the controlling phase. Also Hyks et al. (2009) observed that for APC residues from MSWI the solubility of $\text{Cu}(\text{OH})_2$ may be the controlling phase at pH > 10. Zhang et al. (2008a) showed that for MSWI bottom ash the simulating of Cu leaching is mainly dependent on precipitation/dissolution reactions, since surface complexation had little effect on the obtained curves. This study showed that at pH 5–7 the controlling phase is $\text{Cu}_2\text{CO}_3(\text{OH})_2$, and at pH above 7 by CuO. The modelling results over predicted the experimental leaching values for pH below 5. They suggested that surface precipitation and adsorption by dissolved organic carbon (DOC) may play an important role. Moreover, Dijkstra et al. (2006) indicated that the leaching of Cu from MSWI bottom ash is well described by surface complexation to Fe and Al (hydr)oxides. The mineral malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) is the controlling phase at pH above 8, but not for lower pH. Model predictions showed again that Cu solubility is strongly determined by its complexation with dissolved humic and fulvic acids, which are the major reactive components of DOC in MSWI bottom ash leachates. The Cu complexation with DOC is important in all pH range, with the exception of pH above 12. The tenorite (CuO) seems to be not important when DOC complexation is considered. It should be noted that these conditions are often observed for MSWI bottom ash, but not for APC residues. Moreover, Dijkstra et al. (2008) suggested that $\text{Cu}(\text{OH})_2(\text{s})$ should be considered the controlling phase at pH > 8.

3.3. The influence of pH on the leaching behaviour of inorganics associated with salts

Besides the toxic heavy metals analysed in the previous section, other elements are also important for understanding the leaching behaviour of the APC residues. In this section Na, K, Ca, Cl^- and SO_4^{2-} will be considered, since they are major species in the leaching solutions.

Many inorganic salts of Na and K are thermally stable (NaCl , KCl are fairly volatile), and therefore only a moderate part of the feed stock will be volatilized during incineration. Indeed, the major fraction will be in the bottom ash bounded to silicates. X-ray powder diffraction analysis of APC residues showed that both Na and K are mainly in the form of chloride salts (Quina et al., 2008a). The total elemental content (TC) of Na in the five samples was in the range of $27.8\text{--}33.1 \text{ g kg}^{-1}$ and for K from 24.2 to 30.2 g kg^{-1} . Fig. 4a and b depicts TC, the total availability (TA) and the experimental data obtained from pH static tests for Na and K, respectively. From those figures, the behaviour of Na and K appears to be independent of the pH of the solution. These are the expected

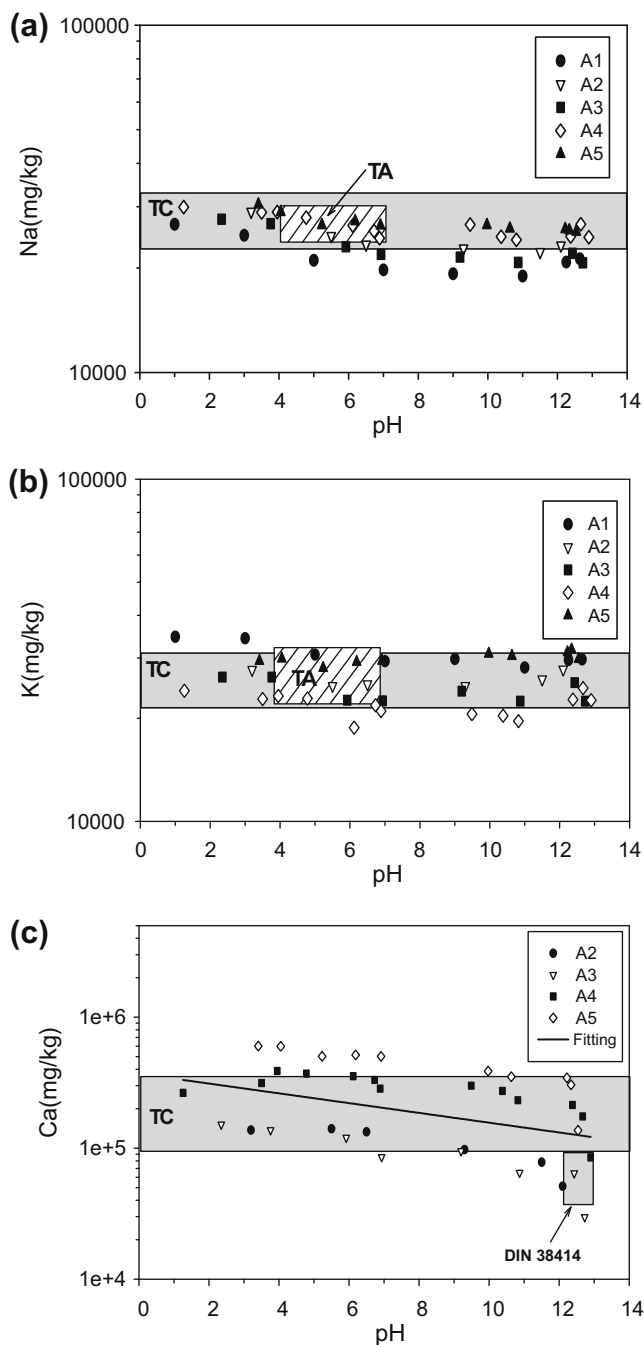


Fig. 4. Influence of pH on the leaching behaviour of (a) Na; (b) K; and (c) Ca.

results once, as referred above, Na and K are present in APC residues mainly as chloride salts. However, if these data are carefully observed a slight increase in the amounts of both alkaline metals is detected as the pH decreases, which may be due to the possibility of these elements being present as less soluble components, e.g. silicates, or being desorbed from negatively charged surfaces. It should be noted that besides the condensation products, due to the temperature decrease in the flue gas stream, the APC residues also contain small particles formed in the combustion chamber and carried over by the gases. The released quantities of Na and K from NaCl and KCl mineral are not limited by their solubility, since these phases are highly soluble. However, the experimental results point out the presence of some solubility controlled specie(s), namely in the form of silicates. Analogous patterns for Na and K were deter-

mined by Eighmy et al. (1995) for ESP ash from MSWI, where they pointed out that these elements are roughly completely dissolved and pH-independent. Other studies indicated the leaching of MSWI bottom ash major species such as Na and K (Meima and Comans, 1997a,b; Dijkstra et al., 2006). In fact, it has been recognized that Na, for example, reveals leaching behaviour roughly independent of pH and with rapid dissolution, mainly from halite (NaCl). However, Dijkstra et al. (2006) showed that sodium exhibits a rapid concentration raise followed by a much slower release (mainly as consequence of kinetically controlled dissolution of less soluble phases).

Calcium is the major element in the APC residues from MSWI, and although their earth-alkali salts can be thermally volatilized at the temperatures taking place in the combustion chamber, the larger contribution is the lime added in the semi-dry scrubber units. In fact, the APC residues considered in this study also contain the additives introduced in the semi-dry scrubber system (slurry of lime and activated carbon). Thus, besides the residue may contain Ca as a matrix constituent of the fly ashes carried over from the boiler, it also contains the reaction products of the neutralization or even unreacted lime. Fig. 4c shows the results obtained for Ca as a function of pH, where the total elemental content (from 243 up to 361 g kg⁻¹) was also included as well as the range obtained through DIN 38414 tests (33.8–96.7 g kg⁻¹ when 12.4 < pH < 12.9). These data show that Ca solubilization decreases as pH increases. From previous mineralogical characterization through XRD, the main calcium phases identified in the APC residues under consideration are: CaOHCl, CaCO₃, Ca(OH)₂, CaSO₄ and aluminium silicates (e.g. Ca₂Al₂SiO₇) (Quina et al., 2008a). Eighmy et al. (1995) characterized the speciation and leaching behaviour of ESP ash from a MSW incinerator, and although several mineral were identified for Ca, its leaching behaviour as a function of pH was described as solubility controlled, being anhydrite (CaSO₄) the unique mineral used as the controlling phase. For similar residues, Van der Bruggen et al. (1998) found gypsum (CaSO₄·2H₂O) as the controlling phase over the entire pH range. However, hydroxyapatite (Ca₃(PO₄)₂), calcite (CaCO₃) and dolomite (CaCO₃·MgCO₃) may be considered as controlling minerals for high pH. Astrup et al. (2006a,b) showed that for APC residues, gypsum (CaSO₄·2H₂O) may predict Ca solution concentration at pH values below 9.5. For pH above 9.5, ettringite is likely the controlling phase. For the semi-dry residues, portlandite (Ca(OH)₂) shall be the controlling solid at pH 12.5. Calcite (CaCO₃) was oversaturated at pH values above 8, which may indicate slow reaction kinetics. Yan et al. (2008) indicated for MSWI fly ash that calcium at pH 0–12 is in the solution mostly as the Ca²⁺ and CaCl⁺, and CaOH at pH 12–13. The controlling solids for Ca may be CaSO₄·2H₂O (at pH 0–14) and Ca₂PO₄(OH). In this study also ettringite Ca₆Al₂(SO₄)₃12(OH)·26H₂O (at pH 11–13) is mentioned as playing a role, as well as Ca(OH)₂ (at pH 13–14). For MSWI bottom ash, Dijkstra et al. (2006) mentioned gypsum as solubility controlling phase for pH 4–8, calcite at pH 8–12 and referred to that ettringite might be important at pH 10–12. Also other studies identified ettringite as controlling solid (Meima and Comans, 1997a,b). Dijkstra et al. (2006) evaluated the influence of time in the leaching behaviour and concluded that the steady state of Ca concentrations was not obtained after 168 h in the range of pH 10–12. Thus, a kinetic control on the precipitation of ettringite may occur. Moreover, calcite may also precipitate at pH above 10. An important conclusion strengthened in this study is the fact that the CO₂ uptake may lead to all ettringite solubilization, being calcite a possible reaction product.

Chloride is present in APC residues mainly as a reaction product formed in the semi-dry scrubbing units that condensates on the fly ash surface particles (CaOHCl), as well as in the form of NaCl and KCl (Quina et al., 2008a). The chloride concentrations in these

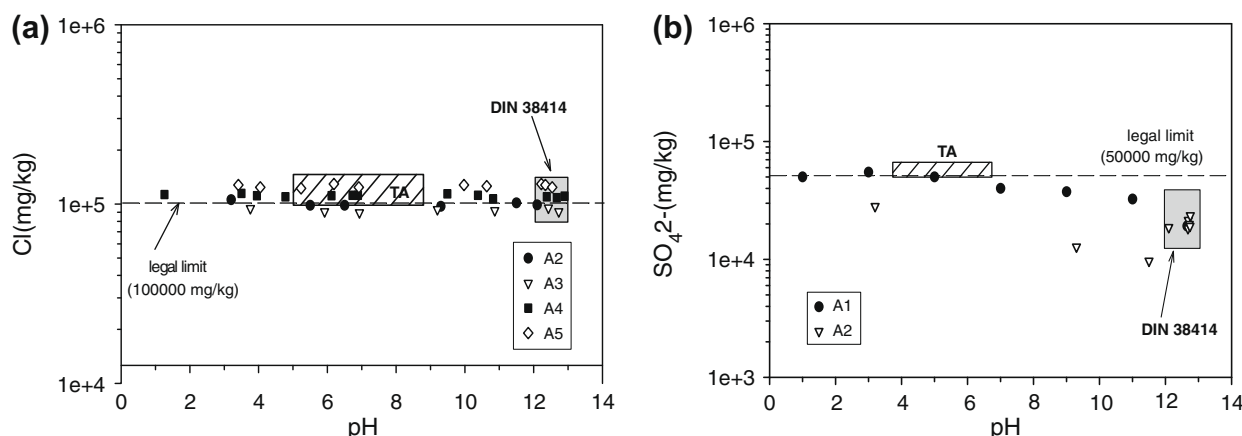


Fig. 5. Influence of pH on the leaching behaviour of (a) Cl^- ; and (b) SO_4^{2-} .

APC residues are in the range of $101.1\text{--}138.3\text{ g kg}^{-1}$, which correspond to more than 10% of the overall mass. Fig. 5a shows the behaviour of chloride (Cl^-) as a function of pH, and the concentration seems to be independent of the pH variation. The amounts measured on total availability (TA) and DIN 38414 leachates are in agreement with the results observed in the pH static test, being possible to conclude that dissolution of this anion is only availability-controlled. Indeed, its behaviour corresponds to the one expected for the very soluble mineral phases: NaCl, KCl and CaOHCl, which were well identified in the solid particles through XRD analysis. It is important to note that chloride concentrations exceeded the regulatory threshold of $100,000\text{ mg kg}^{-1}$ in almost all cases. In literature, the leaching behaviour of chloride is always described as an availability-controlled element, since it is rapidly and completely dissolved for all pH values (Eighmy et al., 1995; Meima and Comans, 1997a,b; Sabbas et al., 2003; Hyks et al., 2009).

The sulphate leaching behaviour as a function of pH is represented in Fig. 5b, and in this case a few results were obtained mainly due to analytical difficulties. The measurement of sulphate ion was performed through ionic chromatography, by using a selective column for F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} . Thus, in order to obtain overall reliable measurement through this technique, the total anions in the liquid sample should not exceed 300 mg L^{-1} . However, due to the high concentration of chlorides, often the peak of SO_4^{2-} was not detected. According to our previous characterization through X-ray fluorescence, sulphur was detected as a major element and, by using X-ray powder diffraction, anhydrite (CaSO_4) was the unique mineral identified that contains S. The results indicated in Fig. 5b shows that the sulphates concentration increases as pH decreases. A regulatory threshold of $50,000\text{ mg kg}^{-1}$ is imposed for this anion, which is not reached in the leachates of DIN 38414. Eighmy et al. (1995) indicated that for ESP ash from MSWI, sulphate shows pH-dependent dissolution phenomena and solid-phase control, and anhydrite (CaSO_4) was the best calcium mineral to describe sulphate leaching mainly at pH 6–10. For different APC residues from MSWI, Astrup et al. (2006a,b) found that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) solubility matches the sulphate concentration at pH below 9–10 and as our results indicate, at pH above 9–10, SO_4^{2-} concentrations decreases. In this case, ettringite may be the controlling solid phase (as well as for Al and Ca). The solid solution (Ba,Ca) SO_4 may play a role in the solubility of sulphate. For MSWI bottom ash, Dijkstra et al. (2006) pointed out that SO_4^{2-} may be almost pH-independent at pH 4–8, being its solubility limited by gypsum. However, at higher pH values gypsum becomes undersaturated, and the possible controlling solid is now ettringite. Also for MSWI bottom ash, Meima and Comans (1997a,b) have indicated

that SO_4^{2-} is solubility controlled mainly by gypsum and for high pH values by ettringite.

4. Conclusions

This study aims to evaluate the influence of pH on the leaching behaviour of inorganic species (Pb, Cd, Zn, Cr, Cu, Ni, Na, K, Ca, Cl^- , SO_4^{2-}) from a combined MSWI APC residue. The experimental results showed that 48 h were enough to obtain pH-equilibrium conditions. The acid neutralization capacity (ANC) for this residue is $6.2\text{--}6.8\text{ meq g}^{-1}$ for pH = 7 and $10.1\text{--}11.6\text{ meq g}^{-1}$ when the end point is pH = 4. These significant ANC values reveal that high resistance to pH variations should be expected.

From the leaching behaviour of the toxic heavy metals as a function of pH, it was possible to conclude that the amphoteric behaviour is only observed for Pb and Zn. For Pb the minimum solubility is observed for pH close to 9, and for Zn the minimum is around pH 10. Taking into account the legal limits established, the amphoteric behaviour of Pb is extremely negative, since the legal limit may be largely exceeded. Indeed, due to the high ANC of the residue, compliance with the legal limit of 20 mg kg^{-1} for Pb will be hardly ever observed under ambient condition. Thus, a treatment before disposed of in landfill sites is required (Quina et al., 2008b). For Zn, compliance with the legal limit of 100 mg kg^{-1} was always observed, in spite of the amphoteric behaviour of this element. For Cu and Ni the characteristics of the residue (high pH and ANC) are favourable in respect to the amount released for the natural pH of the residue (pH higher than 12), since the released amount of these elements decreases as the pH increases. Only in case of extreme acidic conditions, Ni and Cu may become problematic elements. In respect to Cr-total, the legal limit of 50 mg kg^{-1} was not exceeded. Nevertheless, the limit of Cr(VI) is easily exceeded, being then necessary to discriminate Cr(total) from Cr(VI).

Concerning Na and K, the influence of pH is minimal, and the total content is almost completely released in the pH range tested. For Ca (the major element of the residue) an influence of pH is detected, and the released amount increases as the pH decreases. The behaviour observed for Cl^- is similar to Na and K, since in this case the leached amount is total for all pH range. The concentration of this anion may be of concern, once the legal limit ($100,000\text{ mg kg}^{-1}$) was often overcome. The behaviour for sulphate anion slightly depends on pH, and its solubility tends to decrease as pH increases.

The experimental data indicated in this study should be complemented by geochemical modelling, in order to clearly identify possible solubility-controlling minerals and provide information

for environmental impact assessment or risk analysis. In the last years, considerable progresses have been made in this domain.

As a general conclusion of this work, one may state that for the hazardous APC residues produced in a Portuguese MSW incinerator, the species of major concern are lead and chloride. Concerning chromium, it is important to evaluate the amount of Cr(III) and Cr(VI) instead Cr-total. The high ANC values have a negative effect for Pb, since the legal limit is easily exceeded whenever the residue is in contact with water. On the other hand, leaching of elements like Cd, Ni and Cu is limited by the high pH of APC residues, and as long as the material keeps its ANC, the risk of mobilization of these elements is low.

References

- Abbas, Z., Steenari, B.-M., 2001. A study of Cr(VI) in ashes from fluidized bed combustion of municipal solid waste: leaching, secondary reactions and the applicability of some speciation methods. *Waste Manage.* 21, 725–739.
- Allison, J.D., Brown, D.S., Novo-Gradac, K.J., 1991. MINTEQA2/PRODEFA2. A Geochemical Assessment Model for Environmental Systems. Version 3.0 User's Manual. US Environmental Protection Agency, Athens, GA.
- Astrup, T., Rosenblad, C., Trapp, S., Christensen, T., 2005. Chromium release from waste incineration air-pollution-control residues. *Environ. Sci. Technol.* 39, 3321–3329.
- Astrup, T., Dijkstra, J.J., Comans, R.N.J., van der Sloot, H.A., Christensen, T.H., 2006a. Geochemical modeling of leaching from MSWI air-pollution-control residues. *Environ. Sci. Technol.* 40, 3551–3557.
- Astrup, T., Mosbæk, H., Christensen, T.H., 2006b. Assessment of long-term leaching from waste incineration air-pollution-control residues. *Waste Manage.* 26, 803–814.
- Baciacchi, R., Poletti, A., Pomi, R., Prigione, V., Von Zedwitz, V., Steinfeld, A., 2006. CO₂ sequestration by direct gas–solid carbonation of air pollution control (APC) residues. *Energ. Fuels* 20, 1933–1940.
- Bosshard, P.P., Bachofen, R., Brandl, H., 1996. Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. *Environ. Sci. Technol.* 30, 3066–3070.
- Chiang, K.-Y., Tsai, C.-C., Wang, K.-S., 2009. Comparison of leaching characteristics of heavy metals in APC residue from an MSW incinerator using various extraction methods. *Waste Manage.* 29, 277–284.
- Cornelis, G., Johnson, C.A., Van Gerven, T., Vandecasteele, C., 2008. Leaching mechanisms of oxyanionic metalloids and metal species in alkaline solid wastes: a review. *Appl. Geochem.* 23, 955–976.
- Crannell, B.S., Eighmy, T.T., Krzanowski, J.E., Eusden Jr., J.D., Dhaw, E.L., Francis, C.A., 2000. Heavy metal stabilization in municipal solid waste combustion bottom ash using soluble phosphate. *Waste Manage.* 20, 135–148.
- Dijkstra, J.J., van der Sloot, H.A., Comans, R.N.J., 2002. Process identification and model development of contaminant transport in MSWI bottom ash. *Waste Manage.* 22, 531–541.
- Dijkstra, J.J., van der Sloot, H.A., Comans, R.N., 2006. The leaching of major and trace elements from MSWI bottom ash as a function of pH and time. *Appl. Geochem.* 21, 335–351.
- Dijkstra, J.J., Meeussen, J.C., van der Sloot, H.A., Comans, R.N., 2008. A consistent geochemical modelling approach for the leaching and reactive transport of major and trace elements in MSWI bottom ash. *Appl. Geochem.* 23, 1544–1562.
- Eighmy, T.T., Eusden, J., Krzanowski, J., Domingo, D., Stampfli, D., Martin, J., Erickson, P., 1995. Comprehensive approach toward understanding element speciation and leaching behavior in municipal solid waste incineration electrostatic precipitator ash. *Environ. Sci. Technol.* 29, 629–646.
- Fallman, A.M., 1997. Performance and design of the availability test for measurement of potentially leachable amounts from waste materials. *Environ. Sci. Technol.* 31, 735–744.
- Fischer, J., Lorenz, W., Bahadir, M., 1992. Leaching behaviour of chlorinated aromatic compounds from fly ash of waste incinerators. *Chemosphere* 25, 543–552.
- Geysen, D., Imbrechts, K., Vandecasteele, C., Jaspers, M., Wauters, G., 2004. Immobilization of lead and zinc in scrubber residues from MSW combustion using soluble phosphates. *Waste Manage.* 24, 471–481.
- Hammy, F., Mercier, G., Blais, J.-F., 2005. Removal of lead in APCR leachates from municipal solid waste incinerator using peat moss in a batch counter-current sorption process. *Hydrometallurgy* 80 (4), 232–240.
- Hsi, H.-C., Yu, T.-H., 2007. Evaluation of the leachability of polychlorinated dibenzop-dioxins and dibenzofurans in raw and solidified air pollution control residues from municipal waste incinerators. *Chemosphere* 67, 1434–1443.
- Hyks, J., Astrup, T., Christensen, T.H., 2009. Long-term leaching from MSWI air-pollution-control residues: leaching characterization and modeling. *J. Hazard. Mater.* 162, 80–91.
- IAWG (International Ash Working Group). Chandler, A.J., Eighmy, T.T., Hartlén, O., Kosson, D., Sawell, S.E., van der Sloot, H., Vehlouw, J., 1997. Municipal solid waste incinerator residues. *Studies in Environmental Science*, vol. 67. Elsevier Science, Amsterdam.
- Ibáñez, R., Andrés, A., Viguri, J.R., Ortiz, I., Irabien, J.A., 2000. Characterisation and management of incinerator wastes. *J. Hazard. Mater.* A79, 215–227.
- Iretskaya, S., Nzihou, A., Zahraoui, C., Sharrock, P., 1999. Metal leaching from MSW fly ash before and after chemical and thermal treatments. *Environ. Prog.* 18, 144–148.
- Johnson, C., Kersten, M., Ziegler, F., Moor, H., 1996. Leaching behaviour and solubility – controlling solid phases of heavy metals in municipal solid waste incinerator ash. *Waste Manage.* 16, 129–134.
- Johnson, C.A., Kaeppli, M., Brandenberger, S., Ulrich, A., Baumann, W., 1999. Hydrological and geochemical factors affecting leachate composition in municipal solid waste incinerator bottom ash. *J. Contam. Hydrol.* 40, 239–259.
- Kersten, M., Moor, H.C., Johnson, C.A., 1997. Speciation of trace metals in leachate from a MSWI bottom ash landfill. *Appl. Geochem.* 12, 675–683.
- Kersten, M., Schulz-Dobrick, B., Lichtensteiger, T., Johnson, C.A., 1998. Speciation of Cr in leachates of a MSWI bottom ash landfill. *Environ. Sci. Technol.* 32, 1398–1403.
- Kida, A., Noma, Y., Imada, T., 1996. Chemical speciation and leaching properties of elements in municipal incinerator ashes. *Waste Manage.* 16, 527–536.
- Kosson, D.S., van der Sloot, H.A., Sanchez, F., Garraabrants, A.C., 2002. An integrated framework for evaluating leaching in waste management and utilization of secondary materials. *Environ. Eng. Sci.* 19, 159–204.
- Li, L.Y., Ohtsubo, M., Higashi, T., Yamaoka, S., Morishita, T., 2007. Leachability of municipal solid waste ashes in simulated landfill conditions. *Waste Manage.* 27, 932–945.
- Meima, J., Comans, R.N.J., 1997a. Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash. *Environ. Sci. Technol.* 31, 1269–1276.
- Meima, J., Comans, R.N.J., 1997b. Overview of geochemical processes controlling leaching characteristics of MSWI bottom ash. *Stud. Environ. Sci.* 71, 447–457.
- Meima, J., Comans, R.N.J., 1998. Application of surface complexation/precipitation modeling to contaminant leaching from weathered municipal solid waste incinerator bottom ash. *Environ. Sci. Technol.* 32, 688–693.
- Meima, J., Comans, R.N.J., 1999. The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering. *Appl. Geochem.* 14, 159–171.
- Meima, J.A., van der Weijden, R.D., Eighmy, T.T., Comans, R.N.J., 2002. Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum. *Appl. Geochem.* 17, 1503–1513.
- Mizutani, S., Yoshida, T., Sakai, S., Takatsuki, H., 1996. Release of metals from MSW I fly ash and availability in alkali condition. *Waste Manage.* 16, 537–544.
- Mizutani, S., Takatsuki, H., Sakai, S.-I., Watanabe, N., 2007. Influence of particle size preparation of MSW incineration residues on heavy metal leaching behavior in leaching tests. *Environ. Sci.* 13, 363–370.
- Nagib, S., Inoue, K., 2000. Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching. *Hydrometallurgy* 56, 269–292.
- Polettini, A., Pomi, R., Sirini, P., Testa, F., 2001. Properties of Portland cement – stabilised MSWI fly ashes. *J. Hazard. Mater.* B88, 123–138.
- Quina, M.J., 2005. Processos de Inertização e Valorização de Cinzas Volantes-Incinerção de Resíduos Sólidos Urbanos (Treatment and Valorization of APC Residues – Municipal Solid Waste Incineration). PhD thesis. University of Coimbra, Portugal.
- Quina, M.J., Santos, R.C., Bordado, J.C.M., Quinta Ferreira, R.M., 2008a. Characterization of air pollution control residues produced in a municipal solid waste incinerator in Portugal. *J. Hazard. Mater.* 152, 853–869.
- Quina, M.J., Bordado, J.C.M., Quinta Ferreira, R.M., 2008b. Treatment and use of air pollution control residues from MSW incineration: an overview. *Waste Manage.* 28, 2097–2121.
- Sabbas, T., Polettini, A., Pomi, R., Astrup, T., Hjelm, O., Mostbauer, P., Cappai, G., Magel, G., Salhofer, S., Speiser, C., Heuss-Assbichler, S., Klein, R., Lechber, P., 2003. Management of municipal solid waste incineration residues. *Waste Manage.* 23, 61–88.
- Shim, Y.-S., Rhee, S.-W., Lee, W.-K., 2005. Comparison of leaching characteristics of heavy metals from bottom and fly ashes in Korea and Japan. *Waste Manage.* 25, 473–480.
- Sperling, M., Xu, S., Welz, B., 1992. Determination of chromium(III) and chromium(VI) in water using flow injection on-line preconcentration with selective adsorption on activated alumina and flame atomic absorption spectrometric detection. *Anal. Chem.* 64, 3101–3108.
- Van der Bruggen, B., Vogels, G., Van Herck, P., Vandecasteele, C., 1998. Simulation of acid washing of municipal solid waste incineration fly ashes in order to remove heavy metals. *J. Hazard. Mater.* 57, 127–144.
- van der Sloot, H.A., Heasman, L., Quevaullier, Ph., 1997. Harmonization of leaching extraction tests. *Studies in Environmental Science*, vol. 70. Elsevier Science, Amsterdam.
- van der Sloot, H.A., Kosson, D.S., Hjelm, O., 2001. Characteristics, treatment and utilization of residues from municipal waste incineration. *Waste Manage.* 21, 753–765.
- van der Sloot, H.A., Meeussen, J.C.L., van Zomeren, A., Kosson, D.S., 2006. Developments in the characterisation of waste materials for environmental impact assessment purposes. *J. Geochem. Explor.* 88, 72–76.
- van der Sloot, H.A., van Zomeren, A., Meeussen, J.C.L., Johannes, C.L., Seignette, P., Bleijerveld, R., 2007. Test method selection, validation against field data, and predictive modelling for impact evaluation of stabilised waste disposal. *J. Hazard. Mater.* 141, 354–369.
- Van Herck, P., Van der Bruggen, B., Vogels, G., Vandecasteele, C., 2000. Application of computer modelling to predict the leaching behaviour of heavy metals from

- MSWI fly ash and comparison with a sequential extraction method. *Waste Manage.* 20, 203–210.
- Yan, Z., Jianguo, J., Maozhe, C., 2008. MINTEQ modeling for evaluating the leaching behavior of heavy metals in MSWI fly ash. *J. Environ. Sci.* 20, 1398–1402.
- Yasuhara, A., Katami, T., 2007. Leaching behavior of polychlorinated dibenzo-p-dioxins and furans from the fly ash and bottom ash of a municipal solid waste incinerator. *Waste Manage.* 27, 439–447.
- Youcai, Z., Lijie, S., Guojian, L., 2002. Chemical stabilization of MSW incinerator fly ashes. *J. Hazard. Mater.* 95, 47–63.
- Zhang, H., He, P.-J., Shao, L.-M., Li, X.-J., 2008a. Leaching behavior of heavy metals from municipal solid waste incineration bottom ash and its geochemical modelling. *J. Mater. Cycles Waste Manage.* 10, 7–13.
- Zhang, H., He, P.-J., Shao, L.-M., Lee, D.-J., 2008b. Temporary stabilization of air pollution control residues using carbonation. *Waste Manage.* 28, 509–517.